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Injection Moulding of Silicon Carbide Using an Organic Vehicle Based on a Preceramic Polymer

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Abstract

Large ceramic injection mouldings were prepared using a SiC composition with polycarbosilane and paraffin wax. The material sustained mixing and injection moulding at temperatures up to 230°C. Conventional, modulated pressure and heated sprue techniques were used to produce large sections, some of which were subsequently pyrolysed and sintered. Fired relative densities of 97% were obtained under conditions where the dry compacted powder sintered to 90%.

1 Introduction

Previous work[1] has identified modifications to a ceramic polymer composition suitable for injection moulding in which a transient organic binder is replaced with a polymer which decomposes to silicon carbide. The idea of using polycarbosilane as a binder for silicon carbide was proposed by Yajima[2] and hypostatised by Mutsuddy for extrusion.[3] In the same way Sugawara[4] added polycarbosilane at approximately 40 vol.% to a binder system of ethylene vinyl acetate, wax, dibutyl phthalate and a fatty acid ester for injection-moulding silicon carbide powder. Similarly, Okumara[5] blended polycarbosilane with stearic acid to provide a moulding composition for SiC powder.

By incorporating paraffin wax into the composition, the viscosity is reduced and the danger of temperature-induced crosslinking in the machine is avoided.[1] In the present work, this approach was followed up by using the composition previously developed in an injection-moulding machine to make several components and hence examine the behaviour of the material in the mould-filling and solidification stages.

2 Experimental Stages

The silicon carbide was grade 059S from Superior Graphite Co., Chicago, USA. The powder is shown in Fig. 1 and was equiaxed with irregular shape, with a mean particle size of 0·8 μm. Polycarbosilane (PCS) was supplied by Changsha Institute of Technology, People's Republic of China.

The wax was grade 130/135 from Shell Chemicals UK. The mixture prepared contained 56 vol.% SiC and the composition was 80% SiC, 14% PCS and 6% wax by weight.

Mixing was carried out using a Betol (Luton, Beds, UK) TS40 twin-screw extruder running at 60 rpm with barrel temperatures 190–200–220–210°C feed to exit. When cold, the extrudate was granulated by passing it through the unheated rolls of a twin-roll mill to produce feedstock for the injection-moulding machine.

Viscosity was measured with a Davenport Capillary Rheometer fitted with a 2-mm diameter, 40-mm long die and a 5000 psi pressure transducer. A temperature of 226°C was used and shear rates from 20–150 s^{-1} were studied.

Injection moulding was done on a Negri-Bossi NB90 SM290 machine modified for ceramics use. Three moulds were used producing (i) a centre-gated rectangular bar measuring 15 mm × 10 mm × 113 mm, (ii) an axially gated cylinder measuring 40 mm diameter and 60 mm in length and (iii) a straight-bladed rotor having a diameter of 94 mm with a solid hub. The injection speed was $6{\cdot}7 \times 10^{-5}$ m^3/s. The injection moulding variables are given in Table 1. Examples of these mouldings made with the SiC–PCS blend are shown in Fig. 2.

The bars were made using conventional static pressure moulding with a sprue bush having a minimum diameter of 10 mm. The cylinders were made using a heated sprue which has been described previously.[6,7] The sprue was heated to 210°C before injection and held at that temperature for 300 s which was calculated[8] to be greater than the time needed for the centre of the cylinder to solidify in a mould at 40°C. The rotors were made using either static pressure or modulated pressure at various pressure amplitudes using the procedure described previously.[9]

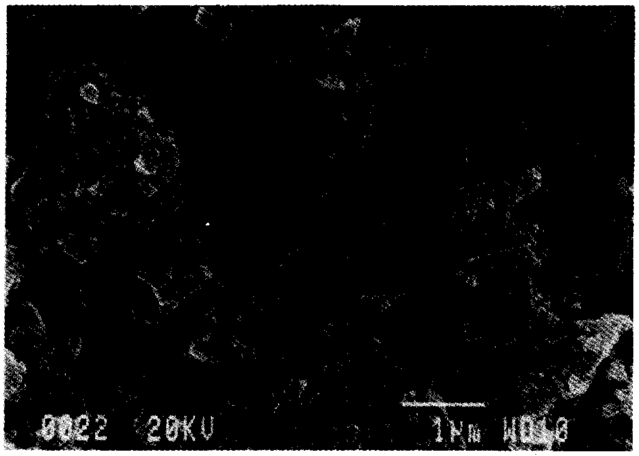

Fig. 1. Scanning electron micrograph of the silicon carbide powder.

The injection-moulding machine was operated with barrel temperatures 210–220–230–230°C feed to nozzle. The mould temperature was varied from 20°C to 50°C and the pressures, which are discussed in Section 3, were varied as shown in Table 1.

Partial pyrolysis of mouldings was carried out in an oxygen-free nitrogen flow of 30 litres/h up to a maximum temperature of 500°C.

Table 1. Injection moulding conditions

Mould temperature (°C)	*Injection pressure (MPa)*	*Hold pressure*[a] *(MPa)*	*Frequency (Hz)*
Rectangular bars; conventional moulding			
20	108	97	–
20	141	54	–
35	141	54	–
40	141	54	–
50	141	54	–
Rotors; conventional moulding			
38	97	54	–
38	108	54	–
38	141	54	–
38	108	32	–
Rotors; modulated pressure moulding			
38	108	71	1
38	108	71	0·7
38	108	85	0·7
38	108	92	0·7
38	108	99	0·7
38	108	106	0·7
38	108	120	1
40	108	92	0·7
Large cylinders; heated sprue moulding			
30	108	76 (3 s) then 15 (until end)	–
30	108	76 (2 s) then 15 (200 s) then 10 (100 s) then 5 (200 s)	–

[a] For modulated pressure moulding, this column gives the amplitude.

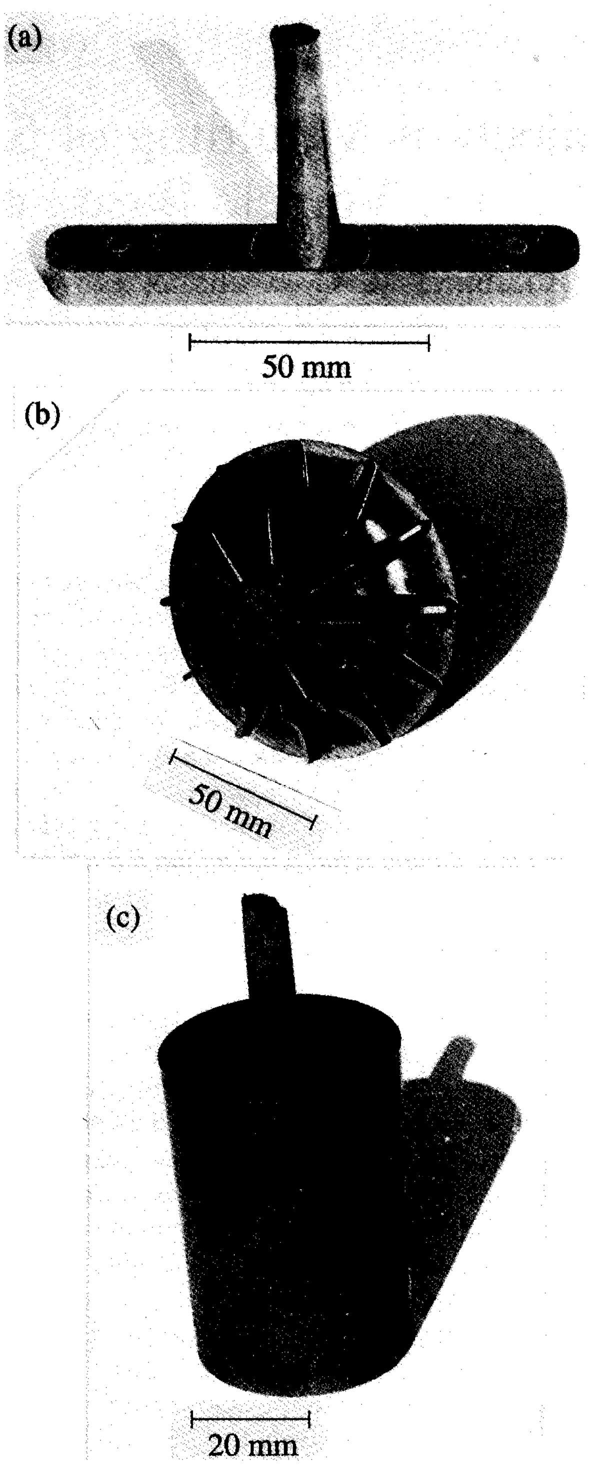

Fig. 2. Injection moulded components: (a) centre-gated rectangular bar, (b) straight-bladed rotor, (c) cylinder.

After initial pyrolysis to 500°C, samples were sintered in a carbon resistance furnace (Jones Vacuum Ltd., Bury, Lancs, UK). The heating rate was 10°C/min to 900°C followed by 5°C/min to 1500°C and a one-hour dwell under vacuum. An argon flow was then established and the temperature was raised to 2050°C at a 5°C/min rate and a 30 min dwell at 2050°C ensued. The density of sintered samples was measured by the Archimedes method in distilled water with a drop of surfactant added.

The sintering behaviour of the pyrolysed bars was compared with that of pressed components of the SiC powder without organic additives. Rectangular bars (8 × 8 × 51 mm) were made by single-ended die pressing at 70 MPa. Bars of the same size were cut from the pyrolysed injection-moulded material. Pairs of bars were companion-fired in a graphite element vacuum furnace (Lenton, Leics, UK) at 15°C/min to 2000°C and held for 0·5 h and 4 h. An argon flow rate of 0·5 litres/min was maintained. Fracture surfaces were examined in a Cambridge S250 scanning electron microscope.

3 Results and Discussion

3.1 Injection moulding

When mixed in the proportions tested previously,[1] the suspension had a higher viscosity at the same powder volume loading. This indicates a slightly higher molecular weight for the new sample of PCS, which is made in the laboratory in batches and is not a commercial product.

The composition of the organic vehicle was therefore changed from that used previously so that the ratio of PCS to wax was 7:3 instead of 4:1 and this gave an apparent viscosity at 121 s^{-1} of 800 Pa s and a flow behaviour index of 0·7 at 226°C. Thus the increase in wax fraction had the effect of making the suspension slightly more Newtonian.

In the previous work,[1] mixing was carried out in solvent. The large quantities of material required for injection moulding favoured mixing by twin-screw extrusion at high temperatures. The success of this process shows that the suspension, based on polycarbosilane, can be compounded in plastics processing machinery. This is a necessary but not sufficient condition for admitting a new material to the injection-moulding machine barrel. The other condition is that the apparent viscosity in the region of 100 s^{-1} should be less than about 1000 Pa s.

The mixture had a low softening point of ≈50°C[1] and this meant that shrinkage in the solid state was low. Although this should mean that residual stresses are reduced, it also leads to the tendency to resist ejection. This was a particular problem with the rectangular bars, 50% of which fractured on ejection because of failure to release the sprue when high hold pressures or mould temperatures were used. Rectangular bars made by conventional moulding with a hold pressure of 54 MPa in a mould at 35°C were free from macroscopic defects in the polished section after moulding (Fig. 3). The dimensional reproducibility of the moulded bars is reflected in the coefficient of variation for the length of the bar, which was 0·1%.

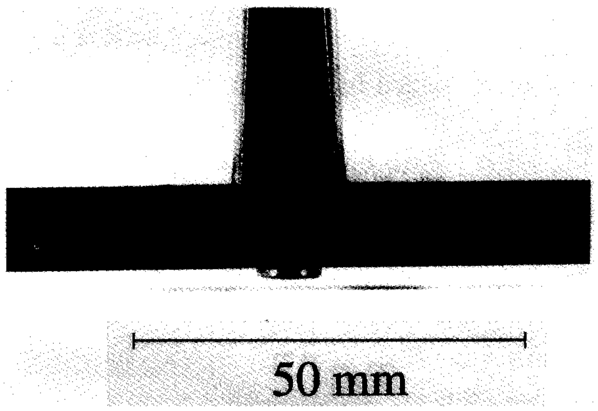

Fig. 3. Polished section of rectangular bar made by the conventional method with a hold pressure of 54 MPa and a mould temperature of 38°C.

Rotors made by conventional moulding were replete with defects over a range of injection and hold pressures as generally observed.[9,10] Figure 4(a) shows the arrangement of defects in a rotor made with a hold pressure of 54 MPa in a mould at 38°C. Variation of the injection pressure did not influence the incidence of defects, which are attributed to the solidification rather than the mould-filling stage. High hold pressures made it very difficult to eject the rotor mouldings without fracture of blades. Modulated pressure rotors with pressure amplitudes in the region 71–92 MPa were free from macroscopic defects in the polished section (Fig. 4(b)) but when the pressure amplitude was increased to 99–120 MPa, large cracks perpendicular to the axis appeared in the hubs of rotors after moulding (Fig. 4(c)). In some cases it was possible to hear and sense the cracking as the rotors were held in the hand after removal from the mould. This phenomenon, attributed to overpacking, has also been reported previously for other systems.[9]

In the frequency region 0·7–1·0 Hz, the frequency had no effect on the appearance of defects. When the frequency was lower than 0·7 Hz, voids appeared even at pressure amplitudes of 120 MPa, an effect that has been attributed to wasted time at the top and bottom of dead centre of piston travel.[11]

Large axially centre-gated cylinders, 40 mm in diameter were made by heated sprue moulding. This method allows large sections to be made without voids at very low pressures. Figure 5 shows the polished section of a cylinder made with a hold pressure of 15 MPa. The sprue was kept molten until the centre of the cylinder was solid. However, the heated sprue process is not yet fully understood and approximately 50% of mouldings showed cracks perpendicular to the axis of the cylinder either on ejection or shortly afterwards. An example is shown in Fig. 6. A similar experience with large heated sprue mouldings with an alumina– polypropylene based system has been reported.[7] It is suggested that this type of cracking arises from the continuing restraint on shrinkage provided by pressure in the liquid core.

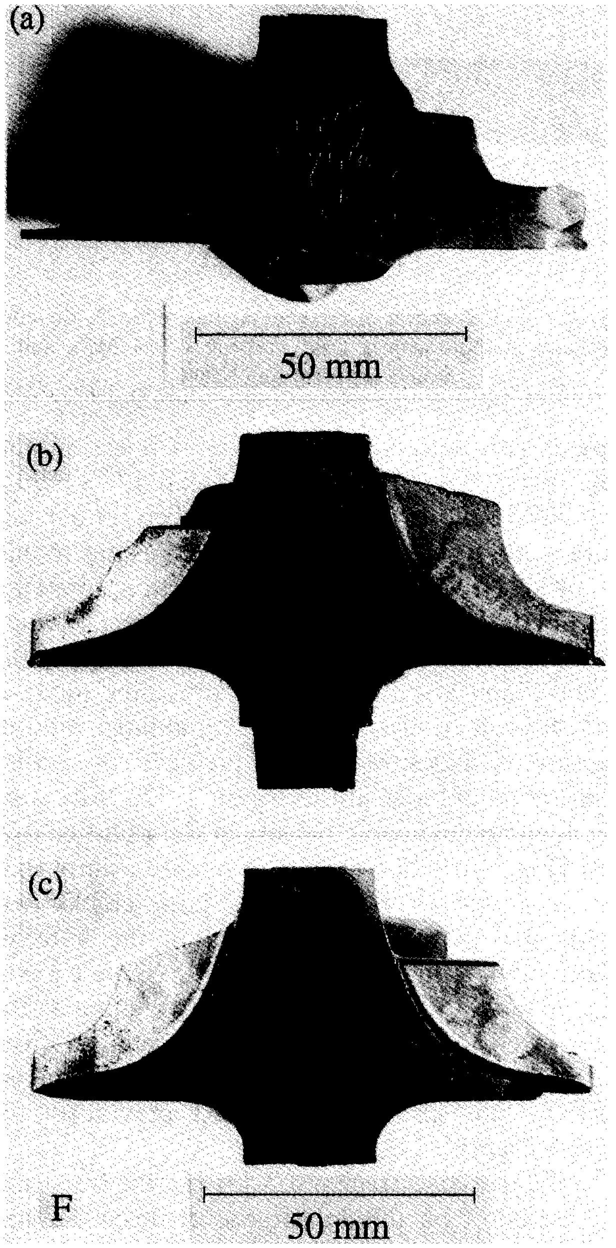

Fig. 4. Polished sections of as-moulded rotors: (a) static pressure 54 MPa, (b) modulated pressure 92 MPa, (c) modulated pressure 120 MPa. The defects are revealed by oblique illumination; no dye was used.

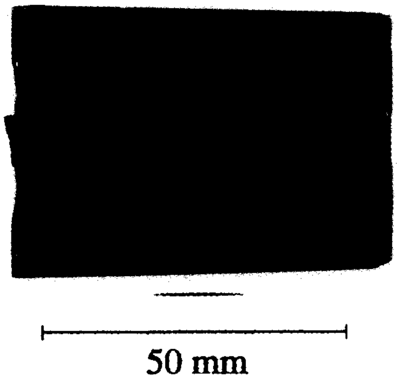

Fig. 5. Section of cylinder made by heated sprue moulding with a 15 MPa hold pressure and mould temperature 30°C.

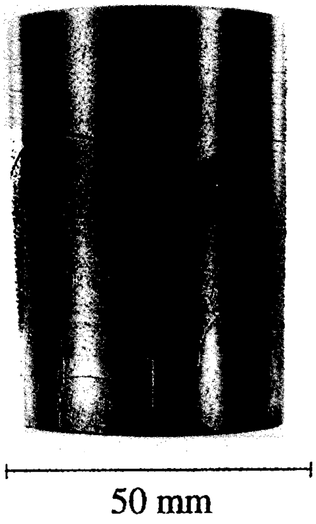

Fig. 6. Cracking in some cylinders made by heated sprue moulding under the same conditions as that in Fig. 5. Flow lines from the axial gating system are also clearly seen in the surface.

3.2 Pyrolysis and sintering of mouldings

Initial pyrolysis was carried out in the temperature range 20–500°C. For the rectangular bar mouldings, the schedule was 60°C/h to 150°C, followed by 2°C/h to 500°C. This produced a weight loss, W_1, of 9·3 ± 0·1 wt%. The bars, which were free from external signs of cracking after moulding, now showed cracks at the junction with the gate. Since the gate had nearly the same diameter as the width of the bar, this region represents the largest overall section. These bars were then broken in half and the sprue was removed before sintering.

Problems were also encountered with the rotor mouldings, which have a much greater section thickness in the hub. These produced a few radial cracks on initial pyrolysis, even at heating rates of 0·5°C/h, which then act as fast transport paths for degradation products. The thinner sections appeared to be sound. A sintered rotor is shown in Fig. 7. There were no external signs of additional defects caused by sintering.

Clearly the overall shrinkage which the component undergoes from the moulded to the sintered state is influenced by the incorporation of a

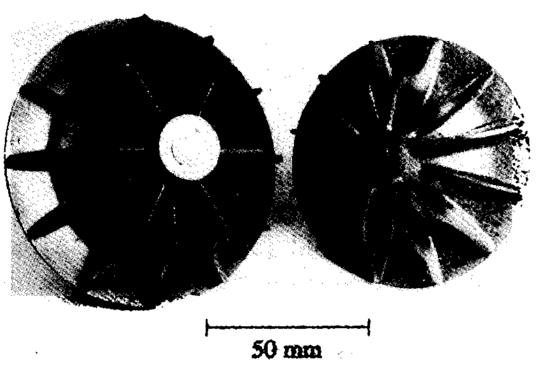

Fig. 7. Rotors, as-moulded (left) and after sintering. Radial cracks appear after pyrolysis of the large section (note the crack at 2 o'clock).

ceramic precursor as binder and by the various weight losses that occur throughout the process. In view of mould tooling costs it is useful to see how well overall shrinkage can be predicted from thermogravimetry.

The average weight loss, W_2, on sintering is made up mainly of the final stage of pyrolysis of the binder, the wax having been expelled earlier. This was 4·1 ± 0·1 wt% measured on 16 samples. The overall weight loss, W_L, is given in terms of the two stages of fractional weight loss by

$$W_L = W_1 + W_2 - W_1 W_2$$

and was 13·0%.

Two stages of shrinkage accompany these processes. The average linear shrinkage after initial pyrolysis was 0·82% measured on the rectangular bar mouldings. The shrinkage attributable to sintering measured on the thickness and width of rectangular bars was 14·0% and 13·8%, respectively. The average overall shrinkage from moulding to sintered body was thus 14·6%.

For samples fired in the Jones furnace, measurement of the sintered density by the Archimedes method in water on 17 bars gave an average of 3122 kg/m^3 with 95% confidence limits based on a '*t*' distribution of ±10 kg/m^3.

Using the crystallographic density of 3218 kg/m^3 for silicon carbide[12] and assuming the sintered body is free of excess carbon or silica, this corresponds to a relative density of 97%, the same value as that obtained by Mutsuddy.[3]

Since the volume of the moulded material accommodates silicon carbide, wax and PCS exclusively, its specific volume is given by

$$V_0 = \sum_{i=1}^{i=3} W_i/\rho_i$$

where W and ρ are weight fractions and density, respectively, giving $V_0 = 4{\cdot}45 \times 10^{-4}$ m^3/kg.

After sintering, the volume is occupied by silicon carbide and voidage, and

$$V_1 = \frac{(1 - W_L)}{\rho_s}$$

where ρ_s is the apparent density of the sintered body and W_L is the overall fractional weight loss. This gives $V_1 = 2{\cdot}787 \times 10^{-4}$ m^3/kg. The overall volumetric shrinkage is therefore 37·4% and since

$$\frac{\Delta L}{L_0} = 1 - \left(1 - \frac{\Delta V}{V_0}\right)^{1/3}$$

the linear shrinkage predicted from weight loss and density measurements is 14·5%. This agrees well with the 14·6% measured from the dimensions of bars.

Table 2. Densities and weight losses for companion-fired injection-moulded and pressed SiC (each value is the average for 2 samples)

		Pressed	*Injection-moulded*
Prefired density (%)		54·3	65·7
Sintered 0·5 h	Weight loss	2·2	4·5
	Density	85·9	93·0
Sintered 4 h	Weight loss	1·7	4·0
	Density	90·0	96·8

The overall weight loss is made up of the 6 wt% and the weight loss on pyrolysis of the PCS. Since the overall loss was 13 wt%, the latter represents 50 wt% based on the initial weight of PCS. This is somewhat larger than the 34 wt% loss from PCS noted previously.[1] However, this excludes weight loss of, for example, native silica from the submicron powder on sintering. A weight loss based on the powder of 1·8 wt% would account for this discrepancy and experience shows that losses from this powder are typically 1–2 wt%. Table 2 shows that the weight losses obtained from sintering compacts of this powder without organic additives were 1·7–2·2%.

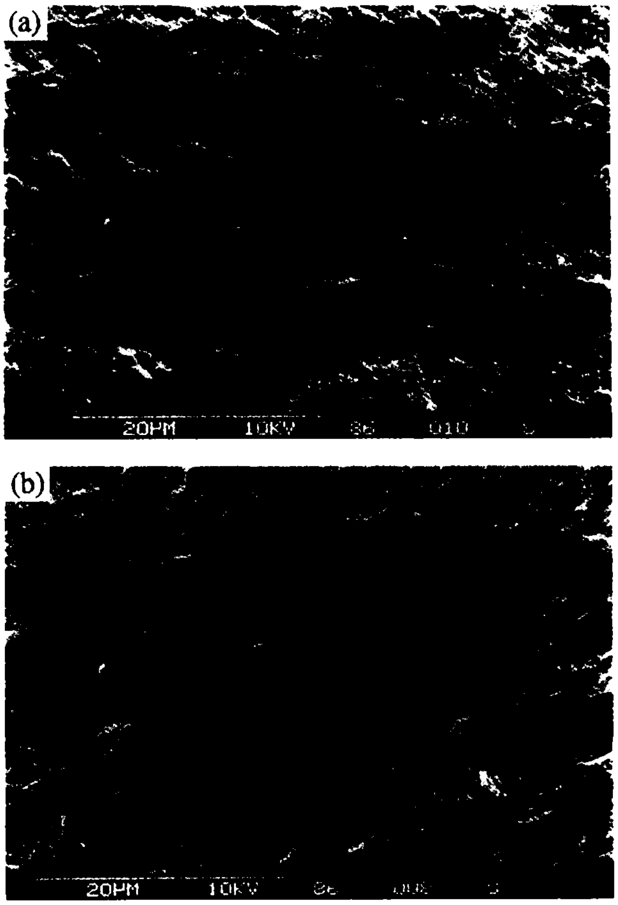

Fig. 8. Scanning electron micrograph of the fracture surfaces of bars companion-fired at 2000°C for 4 h in the Lenton furnace: (a) compacted powder (b) injection-moulded with PCS.

The sintering behaviour of the injection-moulded and pyrolysed bars is compared with that of the die-pressed bars in Table 2. The injection-moulded bars started at a much higher prefired density and reached 97% relative density after 4 h at 2000°C in the Lenton furnace, while pressed bars, fired as companions, reached only 90% relative density. The fracture surfaces of companion-fired bars of both types were examined principally to establish any differences in grain size. Figure 8(a) shows the more extensive porosity in the compacted sample compared with the injection-moulded one (Fig. 8(b)). In both cases, the exaggerated grain growth typical of many silicon carbide artefacts is seen, but there was no evidence of a higher grain size in the sample which had contained PCS.

4 Conclusions

An injection-moulding suspension incorporating a polymeric precursor to silicon carbide diluted with wax can be melt-compounded and injection-moulded at temperatures up to 230°C without premature crosslinking in the machine. Subsequent pyrolysis of large moulded sections produced the same defects that are seen with conventional binder systems, while small sections did not show macroscopic defects. Sintered density was 97% of theoretical and the weight loss and shrinkage were accounted for by the expected SiC residue from the polycarbosilane. Injection-moulded bars, which were companion-fired with compacted bars of the same powder, showed a higher relative density (97%) than the compacted samples (90%). Both samples showed evidence of discontinuous grain growth, but there was no significant difference in grain size.

Acknowledgements

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References

1. Zhang, T. & Evans, J. R. G., The properties of a ceramic injection moulding suspension based on a preceramic polymer. *J. Eur. Ceram. Soc.*, **7** (1991) 405–12.
2. Yajima, S., Special heat resisting materials from organometallic polymers. *Am. Ceram. Soc. Bull.*, **62** (1983) 893–8.
3. Mutsuddy, B. C., Use of organometallic polymer for making parts by plastic forming techniques. *Ceram. Int.*, **13** (1987) 41–53.
4. Sugawara, J., *Ceramic Compositions for Injection Mouldings*. Jpn. Kokai Tokkyo Koho 61053149 17th Mar. 1986, Assgn. Kurasaki Refractories Co.
5. Okumara, M., Moulded silicon carbide products. German Patent 3 409 385, 20th Sept. 1984. Assign. Shin. Nisso Kako Co.
6. Hunt, K. N. & Evans, J. R. G., A heated sprue bush for ceramic Injection moulding. *J. Mater. Sci. Lett.*, **10** (1991) 730–3.
7. Zhang, T. & Evans, J. R. G., The use of a heated sprue in the injection moulding of large sections. *Br. Ceram. Trans.*, **92** (1993) 146–51.
8. Zhang, T. & Evans, J. R. G., The calculation of temperature distributions during the solidification stage in ceramic injection moulding. *J. Am. Ceram. Soc.*, **75** (1992) 2260–7.
9. Zhang, J. G., Edirisinghe, M. J. & Evans, J. R. G., The use of modulated pressure in ceramic injection moulding. *J. Eur. Ceram. Soc.*, **5** (1989) 63–72.
10. Zhang, J. G., Edirisinghe, M. J. & Evans, J. R. G., The control of sprue solidification time in ceramic injection moulding. *J. Mater Sci.*, **24** (1989) 840–8.
11. Zhang, T. & Evans, J. R. G., The solidification of large sections in ceramic injection moulding: II Modulated pressure moulding. *J. Mater. Res.*, **8** (1993) 345–51.
12. JCPDS Powder Diffraction File, Swarthmore, Penn., USA 1974, file 4-0756.